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(54) [Title of the Invention]

Producing method for dihydroxydiphenyl sulfone

(57) [Abstract]

[Problem]

To provide a method capable of industrially faborably co-producing 2,4'-dihyroxydiphenyl sulfone and 4,4'-dihyroxydiphenyl sulfone of a high purity.

[Solving Means]

In producing dihyroxydiphenyl sulfone by a dehydration reaction of a sulfonating agent and a phenol, 2.0 - 4.0 moles of phenol are reacted with 1 mole of the sulfonating agent in o-dichlorobenzene solvent of 2.0 - 6.5 times by weight of a theoretical yield of dihyroxydiphenyl sulfone, and, at the end of the reaction, a proportion of unreacted phenol with respect to the total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid is made 2 - 20 wt.% while the total amount of unreacted phenol and o-dichlorobenzene is made 2.0 - 7.0 times by weight of the theoretical yield of dihydroxydiphenyl sulfone, then 4,4'-dihydroxydiphenyl sulfone is separated by precipitation from the reaction liquid at 80 - 160°C and 2,4'-dihydroxydiphenyl sulfone is isolated from a filtrate.

[Claims]

[Claim 1] A method for producing dihyroxydiphenyl sulfone by a dehydration reaction of a sulfonating agent and a phenol, characterized in reacting 2.0 - 4.0 moles of phenol with 1 mole of a sulfonating agent in o-dichlorobenzene solvent of 2.0 - 6.5 times by weight of a theoretical yield of dihyroxydiphenyl sulfone, then, at the end of the reaction, maintaining a proportion of unreacted phenol with respect to a total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid at 2 - 20 wt.% while maintaining a total amount of unreacted phenol and o-dichlorobenzene at 2.0 - 7.0 times by weight of a theoretical yield of dihydroxydiphenyl sulfone, then separating 4,4'-dihydroxydiphenyl sulfone by precipitation from the reaction liquid at 80 - 160°C and isolating 2,4'-dihydroxydiphenyl sulfone from a filtrate.

[Claim 2] A method according to claim 1, characterized in reacting 2.1 - 2.7 moles of phenol to 1 mole of the sulfonating agent in o-dichlorobenzene solvent of 2.5 - 4.0 times by weight of the theoretical yield of dihyroxydiphenyl sulfone.

[Claim 3] A method according to claim 1 or 2, characterized in, at the end of the reaction, maintaining a proportion of unreacted phenol with respect to the total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid at 2 - 10 wt.% while maintaining the total amount of unreacted phenol and o-dichlorobenzene at 2.5 - 4.5 times by weight of the theoretical yield of dihydroxydiphenyl sulfone.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a method for co-producing 2,4'-dihyroxydiphenyl sulfone and 4,4'-dihyroxydiphenyl sulfone of a high purity.

[0002]

[Prior Technology and Problems to be Solved by the Invention]

2,4'-dihyroxydiphenyl sulfone (hereinafter also called 2,4'-substance) is extremely useful as a color forming agent for thermal paper among various phenolic compounds and is attracting attention recently. For example, in a heat-sensitive recording material containing a leuco dye as a color developing agent and a 2,4'-substance as a main component of a color forming agent, there are provided effects of preventing deterioration of a color developed portion by a plasticizer or by light, and obtaining a color development of a sufficient density even at a low energy.

[0003]

For producing such 2,4'-substance, a method of executing a dehydration reaction of phenol and sulfuric acid employing phosphonic acid or phosphinic acid as a catalyst (JP-A No. 6-107623).

[0004]

In such method, however, though a selectivity for the

2,4'-substance is increased by a reaction utilizing a catalyst, complex separation-purification steps are necessary for separating the 2,4'-substance and a 4,4'-substance (4,4'-dihyroxydiphenyl sulfone) from an obtained isomer mixture (JP-A No. 6-107623).

[0005]

An object of the present invention is to provide a method capable of easily separating the 2,4'-substance and the 4,4'-substance without employing a catalyst and without complex separation-purification steps, thereby industrially faborably co-producing the 2,4'-substance and the 4,4'-substance of a high purity.

[0006]

[Means for Solving the Problems]

The present invention provides a method for producing dihyroxydiphenyl sulfone by a dehydration reaction of a sulfonating agent and a phenol, characterized in reacting 2.0 - 4.0 moles of phenol with 1 mole of a sulfonating agent in o-dichlorobenzene solvent of 2.0 - 6.5 times by weight of a theoretical yield of dihyroxydiphenyl sulfone, then, at the end of the reaction, maintaining a proportion of unreacted phenol with respect to a total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid at 2 - 20 wt.% while maintaining a total amount of unreacted phenol and o-dichlorobenzene at 2.0 - 7.0 times by weight of a theoretical

yield of dihydroxydiphenyl sulfone, then separating 4,4'-dihydroxydiphenyl sulfone by precipitation from the reaction liquid at 80 - 160°C and isolating 2,4'-dihydroxydiphenyl sulfone from a filtrate.

[0007]

The producing method of the invention allows to increase a generating proportion of the 2,4'-substance and the 4,4'-substance to about 50 : 50 in weight ratio, and also to easily isolate the 2,4'-substance and the 4,4'-substance.

[0008]

[Embodiments of the Invention]

A sulfonating agent to be employed in the present invention can be, for example, concentrated sulfuric acid, sulfuric anhydride, fuming sulfuric acid or chlorosulfonic acid. A preferred sulfonating agent is concentrated sulfuric acid.

[0009]

A proportion of the sulfonating agent and phenol is 2.0 - 4.0 moles of phenol with respect to 1 mole of the sulfonating agent, preferably 2.1 - 2.7 moles. A proportion of phenol less than 2.0 moles with respect to 1 mole of the sulfonating agent increases 4,4'-substance and sulfonic acids, while a proportion exceeding 4.0 moles lower the yield and renders efficient separation of the 4,4'-substance and the 2,4'-substance impossible.

[0010]

Also an amount of o-dichlorobenzene is 2.0 - 6.5 times by weight of a theoretical yield of dihydroxydiphenyl sulfone, preferably 2.5 - 4.0 times by weight. An amount of o-dichlorobenzene less than 2.0 times by weight of the theoretical yield of dihydroxydiphenyl sulfone renders efficient separation of the 4,4'-substance and the 2,4'-substance impossible, while an amount exceeding 6.5 times by weight increases the volume, thus being undesirable from economic consideration.

[0011]

The proportion of the sulfonating agent and phenol and the amount of o-dichlorobenzene within the aforementioned ranges allow to increase a generation ratio of the 4,4'-substance and the 2,4'-substance to about 50 : 50 by weight ratio.

[0012]

A reaction temperature is not particularly restricted, but is preferably selected as 150 - 185°C. Also a reaction time is not particularly restricted, but is preferably selected as 3 - 20 hours. The dehydration reaction is promoted by distilling off water from the reaction system, and the reaction is terminated when water is no longer distilled off under heating.

[0013]

A reaction liquid at the end of the reaction is a mixture liquid of a 2,4'-substance, a 4,4'-substance, tri-substances (trihydroxytriphenyl disulfone), sulfonic acids, unreacted

phenol and o-dichlorobenzene, and, in the present invention, the 2,4'-substance and the 4,4'-substance are isolated from such mixture liquid utilizing a difference in solubility at a crystallization temperature. In this operation, a proportion of unreacted phenol with respect to a total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid at the end of the reaction is maintained at 2 - 20 wt.% and a total amount of unreacted phenol and o-dichlorobenzene is maintained at 2.0 - 7.0 times by weight of the theoretical yield of dihydroxydiphenyl sulfone. Preferably the proportion of unreacted phenol with respect to a total amount of unreacted phenol and o-dichlorobenzene is maintained at 2 - 10 wt.% and the total amount of unreacted phenol and o-dichlorobenzene is maintained at 2.5 - 4.5 times by weight of the theoretical yield of dihydroxydiphenyl sulfone.

[0014]

The 2,4'-substance and the 4,4'-substance can be easily isolated in case at the end of reaction the proportion of unreacted phenol with respect to the total amount of unreacted phenol and o-dichlorobenzene and the proportion of the total amount of unreacted phenol and o-dichlorobenzene with respect to the theoretical yield of dihydroxydiphenyl sulfone are within the aforementioned ranges.

[0015]

More specifically, after the reaction is terminated, the

reaction liquid is cooled to 80 - 160°C to precipitate 4,4'-substance which is separated for example by filtration, and then the 2,4'-substance can be isolated from the filtrate. The isolation of the 2,4'-substance from the filtrate can be achieved (1) by further cooling the filtrate to precipitate the 2,4'-substance which is filtered, or (2) by adding water and a basic alkali metal compound to the filtrate to dissolve the 2,4'-substance in the aqueous phase, which is separated from the organic phase and is added with an acid to precipitate the 2,4'- substance that is filtered, or (3) by evaporating and drying the filtrate to obtain the 2,4'-substance.

[0016]

[Examples]

Example 1

To a mixture of 216.4 g (2.3 moles) of phenol and 975 g of o-dichlorobenzene (o-DCB) (3.9 times by weight of the theoretical yield of dihydroxydiphenyl sulfone), 100.0 g (1.0 mole) of 98% sulfuric acid were dropwise added under agitation, and the temperature was then elevated. At about 150°C, the reaction liquid started to boil, and water generated in reaction started to distill out together with o-OCB. The distillate was condensed in a condenser and separated in a trap into two phases, and the lower o-OCB phase was continuously returned to the reaction system. At about 5 hours after the temperature elevation, the reaction system reached a temperature of 180°C,

the water generation was terminated and the amount of water in the trap became constant at 38 ml. At this point, the analysis of the reaction liquid by gas chromatography indicated that the proportion of unreacted phenol with respect to the total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid was 4.8 wt.% and the total amount of unreacted phenol and o-dichlorobenzene was 4.1 times by weight of the theoretical yield of dihydroxydiphenyl sulfone.

[0017]

Also the analysis of the reaction liquid by high-speed liquid chromatography at this point indicated that the reaction liquid had a weight composition of 2,4'-substance : 4,4'-substance : tri-substances = 47.3 : 49.3 : 3.4.

[0018]

Then the reaction liquid was cooled to 120°C, agitated for 30 minutes at this temperature, and the precipitated crystal was filtered to obtain 122.0 g of wet cake (A). The filtrate was further cooled to 25°C, and the precipitated crystal was filtered to obtain 234.8 g of wet cake (B). An analysis of the wet cake (A) by high-speed liquid chromatography provided a result (excluding o-OCB) by weight of 2,4'-substance : 4,4'-substance : tri-substances = 4.8 : 94.3 : 0.9, with an yield to the used sulfuric acid (calculated as dry substance) of 42.4 %. Also an analysis of the wet cake (B) by high-speed liquid chromatography provided a result (excluding o-OCB) by

weight of 2,4'-substance : 4,4'-substance : tri-substances = 85.8 : 8.6 : 5.6, with an yield to the used sulfuric acid (calculated as dry substance) of 46.9 %. The yield of the wet cakes (A) and (B) to the used sulfuric acid (calculated as dry substance) was 89.3 %.

[0019]

Example 2

After the reaction was executed in the same manner as in Example 1, the reaction liquid was cooled to 120°C, and the precipitated crystal was filtered to obtain 122.0 g of wet cake (A). 350 ml of water and 78.0 g of a 48% aqueous solution of NaOH were added to the filtrate, and, after complete dissolution at 50°C, the mixture was separated by standing and the lower organic phase was eliminated. Then 70.0 g of 65% sulfuric acid were added to the aqueous phase, and the precipitated crystal was filtered at 25°C, then rinsed with water and dried to obtain 119 g of a dry product (C). An analysis of the wet cake (A) by high-speed liquid chromatography provided a result (excluding o-OCB) by weight of 2,4'-substance : 4,4'-substance : tri-substances = 4.8 : 94.3 : 0.9, with an yield to the used sulfuric acid (calculated as dry substance) of 42.4 %. Also an analysis of the dry product (C) by high-speed liquid chromatography provided a result by weight of 2,4'-substance : 4,4'-substance : tri-substances = 86.0 : 8.5 : 5.5, with an yield to the used sulfuric acid of 47.1 %. The yield of the

wet cake (A) and the dry product (C) (calculated as dry substance) to the used sulfuric acid was 89.5 %.

[0020]

Comparative Example 1

To a mixture of 282.3 g (3.0 moles) of phenol and 250 g of o-DCB (1.0 times by weight of the theoretical yield of dihydroxydiphenyl sulfone), 100.0 g (1.0 mole) of 98% sulfuric acid were dropwise added under agitation, and the temperature was then elevated. At about 150°C, the reaction liquid started to boil, and water generated in reaction started to distill out together with o-OCB. The distillate was condensed in a condenser and separated in a trap into two phases, and the lower o-OCB phase was continuously returned to the reaction system. At about 5 hours after the temperature elevation, the reaction system reached a temperature of 180°C, the water generation was terminated and the amount of water in the trap became constant at 37 ml. At this point, the analysis of the reaction liquid by gas chromatography indicated that the proportion of unreacted phenol with respect to the total amount of unreacted phenol and o-dichlorobenzene in the reaction liquid was 29.3 wt.% and the total amount of unreacted phenol and o-dichlorobenzene was 1.6 times by weight of the theoretical yield of dihydroxydiphenyl sulfone.

[0021]

Also the analysis of the reaction liquid by high-speed

liquid chromatography at this point indicated that the reaction product had a weight composition of 2,4'-substance : 4,4'-substance : tri-substances = 30.9 : 68.4 : 0.7.

[0022]

Then the reaction liquid was cooled to 120°C, agitated for 30 minutes at this temperature, and the precipitated crystal was filtered to obtain 153.9 g of wet cake (A). The filtrate was further cooled to 25°C, and the precipitated crystal was filtered to obtain 132.7 g of wet cake (B). An analysis of the wet cake (A) by high-speed liquid chromatography provided a result (excluding o-OCB) by weight of 2,4'-substance : 4,4'-substance : tri-substances = 11.7 : 88.1 : 0.2, with an yield to the used sulfuric acid (calculated as dry substance) of 53.5 %. Also an analysis of the wet cake (B) by high-speed liquid chromatography provided a result (excluding o-OCB) by weight of 2,4'-substance : 4,4'-substance : tri-substances = 62.6 : 36.4 : 1.4, with an yield to the used sulfuric acid (calculated as dry substance) of 31.8 %. The yield of the wet cakes (A) and (B) (calculated as dry substance) to the used sulfuric acid was 85.3 %.

[0023]

[Effect of the Invention]

The producing method of the present invention allows to elevate a generation ratio of 2,4'-substance and 4,4'-substance close to 50 : 50 in weight ratio, and also to easily isolate

the 2,4'-substance and the 4,4'-substance, whereby 2,4'-substance and 4,4'-substance of a high purity can be advantageously co-produced industrially.